PATENT SPECIFICATION

(11) **1339930**

NO DRAWINGS

(21) Application No. 16016/71 (22) Filed 20 May 1971

(31) Convention Application No. 39532 (32) Filed 21 May 1970

(31) Convention Application No. 39534 (32) Filed 21 May 1970

(31) Convention Application No. 39535 (32) Filed 21 May 1970

(31) Convention Application No. 133420 (32) Filed 12 April 1971

(31) Convention Application No. 133423 (32) Filed 12 April 1971

(31) Convention Application No. 133425 (32) Filed 12 April 1971 in

(33) United States of America (US)

(44) Complete Specification published 5 Dec. 1973

(51) International Classification C08F 27/00//45/00

(52) Index at acceptance

C3P 4D3B1 4D8 4K8 4P1D 4P3 4P4A 4T2X 8C10 8C13B 8C13C 8C14B 8C20C 8C20D1 8C6B 8C8B 8D2A 8D2B2 8D3A 8D8 8K4 8K8 8P1D 8P1E4 8P3 8P4A 8P6A 8T2A 8T2D 8T2X

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(54) POLYMERIC MATERIALS AND DISPERSIONS CONTAINING THEM

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to polymeric materials, useful as aids for dispersing solid particles in organic liquids, and to the dispersions which contain these polymeric materials.

According to the invention there is provided a polymeric material represented by the structure

$$\left(\mathrm{B{-}X{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{H}{N}}\right)_m\mathrm{{-}Y{-}}\left(\mathrm{\overset{H}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}A}\right)_n$$

where

B is a polymeric segment of one or more ethylenically unsaturated monomers lacking Zerewitinoff hydrogen atoms;

X is the residue of a chain transfer agent;

Y is the residue of a di-, tri- or tetraisocyanate radical;

A is an acid radical which is derived from an acid having a pk_a value of −1 to 6, or a basic radical which is derived from a base having a pk_a value of 5 to 14, or a salt of such a basic radical, and

m and n are 1, 2 or 3, (the total not exceeding 4); provided that when n is 2 or 3, only one of A need be as defined.

The invention also provides a coating composition comprising:

(a) an organic liquid,

(b) a film-forming polymer,

(c) pigment particles dispersed in the liquid, and
(d) at least one polymeric material as specified in the preceding paragraph.

Preferably, the number average molecular weight of the polymeric materials according to the invention is from 500 to 100,000, more preferably 1,000 to 10,000.

The polymeric materials of the invention are useful as aids for dispersing solid particles in organic liquids.

The invention is therefore also directed to dispersions of solid particles in organic liquids, containing one or more polymeric materials of the invention.

The dispersions of the invention are highly resistant to flocculation. This makes them especially useful in preparing coating compositions.

For example, stable organosols of organic polymers such as

polyvinyl chloride
polyvinyl fluoride
polyvinylidene chloride
polyvinylidene fluoride

and

polymers and copolymers of acrylic- and methacrylic acids and their amides, nitriles and esters with alkanols of 1 to 18 carbon atoms,

prepared according to the invention, can in turn be used to prepare coating compositions in which these polymers are the film-forming components.

Polymers and copolymers of acrylic and methacrylic acid esters are preferred as film formers in the coating compositions.

Especially preferred are acrylic graft copolymers represented by the general structure $A' \longrightarrow B'$, where A′ is a copolymeric backbone segment of

(1) an alkyl methacrylate whose alkyl group contains 1—4 carbon atoms,

and

(2) allyl methacrylate (AMA) and/or diethylaminoethyl methacrylate (DEAM),

and B′ is a poly-2-ethylhexyl acrylate (2-EHA), poly(butyl acrylate) (BA) or a copolymer of 2-EHA and BA.

The particles in the dispersions of the invention can also be pigment particles. Illustrative of the pigments which can be used are titanium dioxide, carbon black, zinc oxide, lead titanate, potassium titanate, antimony oxide, lithopone, phthalocyanine blue, toluidine red, quinacridone, "Irgazin" (trade mark) yellow, and ferric hydrates.

The pigment dispersions of the invention are remarkably resistant to flocculation, which gives the paints into which these dispersions are incorporated higher initial gloss, better hiding and tinting strength and makes them resistant to color drift and gloss loss. These pigment dispersions can also be used satisfactorily with many more diverse types of paints than conventional pigment dispersions. Furthermore, a pigment dispersion of the invention can have a significantly higher pigment content, while retaining the same degree of fluidity, than when a conventional aid is used.

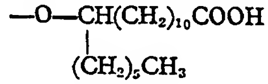
Magnetic oxides such as iron oxide and chromium dioxide can also be the particulate matter in the dispersions. Such compositions are useful for preparing magnetic tape.

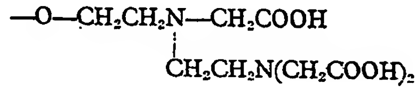
Dispersions containing 40 to 80%, by weight of a magnetic oxide and 0.5—10%, by weight, of a polymeric material of the invention show improved adhesion to the tape substrate and improve the tape's electrical properties.

In one preferred form of the polymeric materials of the invention, A is a carboxyl bearing radical. Still more preferred are those polymeric materials where A is a mercapto-, hydroxy- or carboxy-substituted carboxylic acid radical. For example, A may be

$$\begin{array}{c} CH_2COOH \\ | \\ —S—C—COOH \\ | \\ H \end{array}$$

$$—S—(—CH_2—)—_nCOOH \qquad \text{(where n is 1—3)}$$



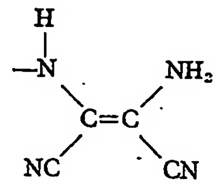


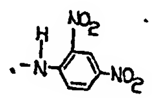
or

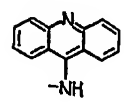
$$-(-CH_2-)-_{10}COOH$$

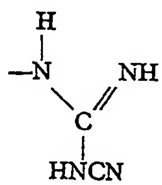
Other preferred polymeric materials according to the invention are those wherein A is an amino-, hydroxy- or mercapto substituted amine or amine salt radical. Especially preferred are those materials where A is

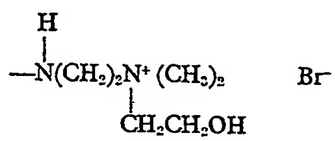
$-NH_2$











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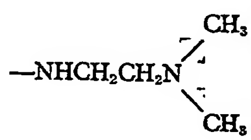


Preferably, B is a polymeric segment of

(a) an ester of acrylic acid (AA) or methacrylic acid (MAA) with an alkanol of 1—18 carbon atoms;
(b) styrene or acrylonitrile
(c) a vinyl ester whose ester moiety contains 2—18 carbon atoms; or
(d) a vinyl ether.

It is also preferred that X be of the formula

$$-S-R-D$$

where R is alkylene of 1—6 carbon atoms, and

D is $-O-$, $-S-$, $-\overset{O}{\overset{\|}{C}}-O-$ or $-NH-$.

Especially preferred are those polymeric materials wherein B is

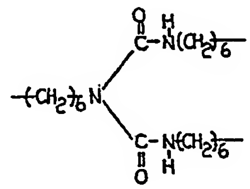
(1) a polymeric segment one of whose monomer units is methyl methacrylate (MMA),

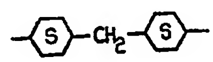
(2) a copolymeric segment of MMA and an ester of AA or MAA with an alkanol of 2—12 carbon atoms,

or

(3) a MMA/2-ethylhexyl (2-EHA) copolymeric segment.

Also especially preferred are those polymeric materials wherein Y is





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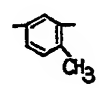
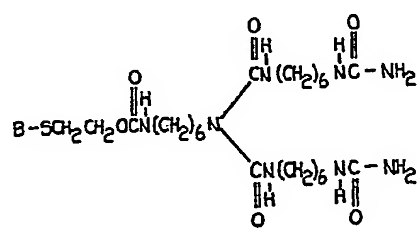


The polymeric materials most preferred are those represented by the structure



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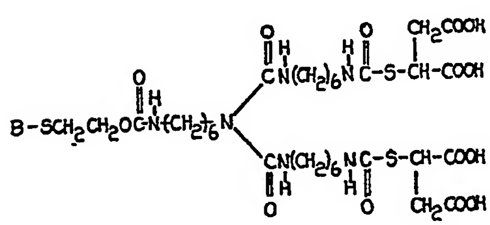
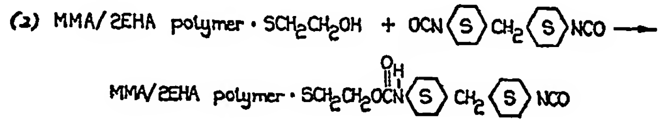
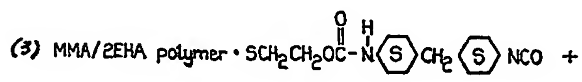


where B is a MMA/2-EHA copolymeric segment.

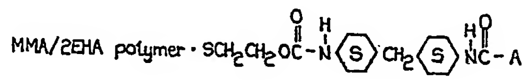
The polymeric materials of the invention can be prepared according to the typical equation

(1) MMA+2EHA+$HSCH_2CH_2OH$→MMA/2EHA polymer · SCH_2CH_2OH





An A group being reactant→



According to this scheme, a suitable organic liquid such as toluene, methethyl ketone, methylisobutyl ketone, butyl acetate, ethyl acetate, benzene, xylene, an ether such as ethylene glycol diethyl ether or Cellosolve acetate, or mixtures of these, is heated at controlled temperature, preferably 50—120°C. Temperature is most easily controlled by using a liquid having a boiling point of 50—120°C. To this organic liquid is then added, over a four-hour period, a solution of the monomer(s) which is to produce the polymeric segment B of the polymeric material, a chain transfer agent bearing a functional group, such as 2-mercaptoethanol, 2-mercaptopropanol or 2-hydroxyethyl disulfide, and a free radical polymerization initiator such as azobisisobutyronitrile.

One chooses the proportions of monomer, chain transfer agent and initiator according to the formula

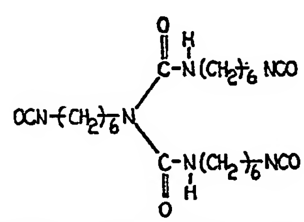
$$MW_n = \frac{\text{total mols monomer}}{\text{total mols transfer agent} + X \text{ (mols of initiator)}}$$

(where X is the number of free radicals per mol of catalyst and MW_n is the number average molecular weight of the polymer desired).

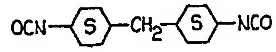
It is desirable that the monomer, chain transfer agent and initiator be in solution. If they are, enough of an appropriate solvent such as Cellosolve (trade mark) acetate or toluene should be added to put them into solution.

The reaction mass is heated at 50—120°C. until reaction is about 95% complete, as determined by viscosity measurements. Ordinarily, at completion, the mass has a Gardner-Holdt viscosity of F to N. Four to five hours of heating is ordinarily enough.

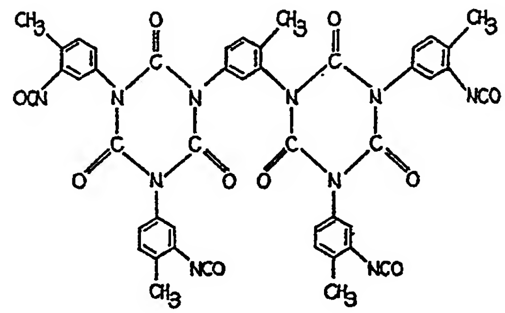
An appropriate di-, tri- or tetraisocyanate, in an amount equimolar to the chain transfer agent, is then added to the reaction mass, still at elevated temperature. Illustrative of isocyanates which can be used are



(Desmodur (trade mark) N, sold by Farbenfabriken Bayer, AG.)



(Hylene (trade mark) W organic isocyanate, sold by E. I. du Pont de Nemours and Company)



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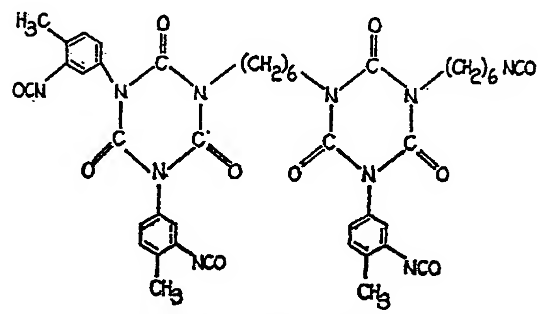


(Desmodur HL, sold by Farbenfabriken Bayer, AG)

and toluene diisocyanate.

A catalyst for the isocyanate reaction is then added to the reaction mass. Illustrative of such a catalyst are dibutyltin dilaurate and tertiary amines such as triethylenediamine. The amount of isocyanate reaction catalyst used is ordinarily 0.5 to about 2%, by weight of the isocyanate used.

The reaction mass is then refluxed until the isocyanate chain transfer agent reaction is complete. This ordinarily takes from 5 to 60 minutes at 80°C.

The reactant which provides the A moiety of the polymeric material is then added as a solution in one of the organic liquids previously mentioned. The amount used is about 0.8—1, preferably 0.95 molar, based on unreacted isocyanate. The reaction mass is then heated at 25—120°C., with stirring, for another 5—60 minutes. Heat need not be applied if mercapto acids or amines which react readily at 25°C., are used.

The A moiety-providing reactant can be any acid having a pk_a value of −1 to 6, or any base having a pk_a value of 5—14.

The dispersing agent can be used in solution, as prepared.

The amine salts can be made by neutralizing the product with acid, by reacting it with an alkyl halide such as methyl iodide, or by other conventional methods.

Preparation of the Dispersions

The dispersions of the invention can be prepared by dissolving from 0.001 to about 2 grams of the polymeric material of the invention per square meter[1] of surface area of the particles to be used, preferably 0.004 to about 0.100 gram per square meter, in

[1] Measured by the Brunauer, Emmett and Teller nitrogen adsorption method described on page 30 of "Colloidal Dispersions" by Earl K. Fischer, published by John Wiley and Sons in 1950.

an organic liquid. If the dispersion is to be made into a paint, this organic liquid must be compatible with the other ingredients.

Illustrative of organic liquids which can be used are aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, ethers, esters, ketones, alcohols and mixtures of these.

An appropriate amount of the particulate material is then added to this solution, which is then subjected to high shear, as by sand grinding, ball milling or roller milling to deagglomerate and disperse the particles.

Alternatively, the dispersions may be prepared by premixing the polymeric material, particulate matter and liquid in a vessel and then grinding the mixture under high shear.

Dispersions of magnetic oxides used for preparing magnetic tape can be made by first preparing a slurry of magnetic oxide in a small amount of a solution of binder resin and deflocculating agent in an organic liquid such as cyclohexanone, methylethyl ketone, methylisobutyl ketone, toluene, dioxane or tetrahydrofuran. This slurry is then ball-milled for 24—48 hours. To the slurry is then added the remainder of the binder resin, solvent and such lubricants, curing agents or other adjuncts as are desired. The resulting dispersion is ball milled for 2—4 hours and is then ready for use.

These dispersions can then be applied to conventional tape substrate usually made of cellulose acetate or Mylar" (trade mark) polyester film*, in the customary way, and then cured, usually by baking for a short period.

The following Examples of the invention are given by way of illustration. All parts and percentages are by weight unless otherwise specified.

Example 1

(A) Toluene (226.7 parts) was placed in a steel reaction kettle, heated to reflux temperature and held there. A solution of 226.7 parts of MMA, 126 parts of 2-EHA, 90.7 parts of toluene, 4.44 parts of 2 mercaptoethanol and 0.903 part of azobisisobutyronitrile was then slowly added to the kettle over a four hour period.

Refluxing was continued as a solution of 0.25 part of azobisisobutyronitrile in 2.5 parts of methylisobutyl ketone was added in three equal portions at intervals of 15 minutes. A water separator was attached to the kettle and refluxing was continued for another 45 minutes to remove water.

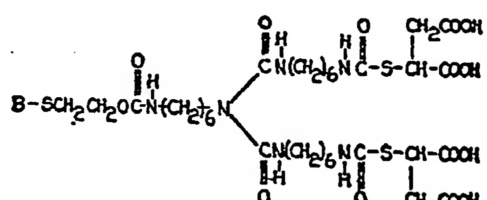
(B) Desmodur N (43.21 parts) was then added to the reaction mass and its container rinsed with 3.78 parts of toluene, which was also added to the mass. The mixture was stirred for 5 minutes.

Dibutyltin dilaurate (0.51 part) was then added and its container rinsed with 1.89 parts of toluene, which was also added to the mixture.

This solution was refluxed for one hour.

(C) The solution was then cooled to about 65°C. and stirred as a solution of 17.09 parts of mercaptosuccinic acid in 120.9 parts of methylethyl ketone was added. The container was rinsed with 3.78 parts of methylethyl ketone, which was also added to the solution. After 30 minutes of stirring at 60—75°C., 0.85 part of acetic anhydride was added.

The resulting product was a solution, 48% solids, of a polymeric material having the general formula



where B is a MMA/2EHA copolymeric segment.

A mixture of 62.5 parts of this solution, 65 parts of phthalocyanine blue pigment, 168 parts of xylene and 66 parts of 2-butoxyethyl acetate was sand-milled to produce

* E. I. du Pont de Nemours and Company. The preferred film is that described in U.S. Patent 3,397,072.

a fluid dispersion. This dispersion was then mixed with a clear thermosetting acrylic enamel vehicle in an amount that provides 2 parts of pigment per 100 parts of polymeric binder. The resulting homogeneous enamel was doctorbladed to glass panel and baked at about 160°C. to give a highly transparent, glossy blue film.

Example 2

Toluene (900 parts) was placed in a reaction flask, heated to reflux temperature and held there. To the toluene was then added, continuously over a 4 hour period, a solution of 1540 parts of MMA, 20.3 parts of 2-mercaptoethanol, 4.1 parts of azobisisobutyronitrile and 300 parts of toluene.

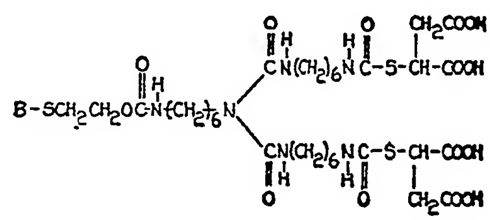
Refluxing was continued while a solution of 3.4 parts of azobiisobutyronitrile in 38 parts of methylisobutyl ketone was added in three equal portions at 15 minute intervals. Refluxing was then continued for another 30 minutes, with water removal.

Desmodur N (197.3 parts) was then added to this solution and its container rinsed with 17 parts of toluene, which was also added.

After the mass had been stirred another 5 minutes, 1.2 parts of dibutyltin dilaurate were added. This solution was heated at reflux temperature for 30 minutes and then cooled to 65°C.

To this solution was then added a solution of 74.1 parts of mercaptosuccinic acid in 520 parts of methylethyl ketone. The container was rinsed with 20 parts of methylethyl ketone, which was also added to the mass. The resulting solution was then stirred for 15 minutes at 60—70°C. and 4 parts of acetic anhydride were added.

The resulting product was a solution, 46% solids, of a polymeric material represented by the formula



where B is poly(MMA).

A mixture of 46 parts of this solution, 70 parts of phthalocyanine blue pigment, 224 parts of xylene and 10 parts of 2-ethoxyethyl acetate was sand-milled. The viscosity of the resulting dispersion was less than 50 centipoise, indicating excellent deflocculation.

The dispersion was mixed with a plasticized poly-(MMA) lacquer containing metallic flake. This lacquer was doctor-bladed on steel and baked at 160°C. to produce a glossy film having excellent appearance.

Example 3

A polymeric material was prepared by the method of Example 2, using 1312 parts of MMA and 280 parts of *n*-butyl acrylate (BA) in place of the MMA used in Example 2.

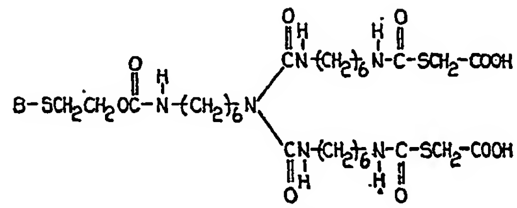
Example 4

A polymeric material was prepared by the method of Example 2, except that the first feed solution was composed of 1120 parts of MMA, 368 parts of lauryl methacrylate (LMA-, 112 parts of acrylonitrile (AN), 22.42 parts of 2-mercaptoethanol, 3.98 parts of azobisisobutyronitrile and 300 parts of toluene.

Example 5

To the intermediate polymeric material prepared in part (B) of Example 1 was added 1 mol of thioglycollic acid for each equivalent weight of unreacted isocyanate.

The mixture was heated at reflux temperature for 1 hour to give a solution of polymeric material represented by the general formula

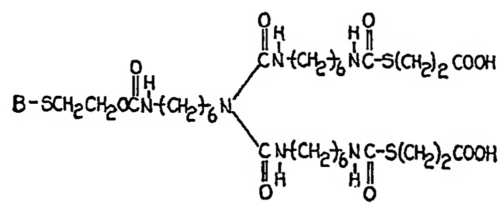


where B is a MMA/2-EHA copolymeric segment.

Example 6

β-mercaptopropionic acid was used in place of the thioglycollic acid used in the previous example.

The product was a polymeric material represented by the general formula



where B is a MMA/2-EHA copolymeric segment.

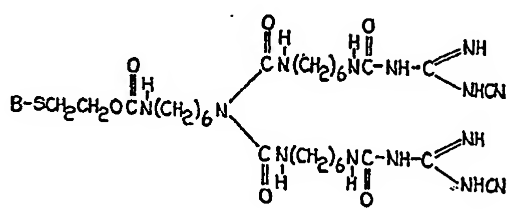
Coating compositions can be prepared with the polymeric materials of Examples 3—6 using the procedures of Example 1 with similar results.

Example 7

2-ethoxyethyl acetate (150 parts) was placed in a reaction vessel. The liquid was heated to 100°C and held there as a solution of 940 parts of MMA, 298 parts of 2EHA, 125 parts of BA, 17.2 parts of 2-mercaptoethanol, 4.9 parts of azobisisobutyronitrile and 500 parts of 2-ethoxyethyl acetate was added continuously over a 4-hour period.

To 1000 parts of this solution were then added 82.5 parts of Desmodur N, 0.5 parts of dibutyltin dilaurate, and 300 parts of 2-ethoxyethyl acetate. The reaction mass was refluxed briefly and then added, over a two-hour period, to a mixture at reflux temperature, of 34 parts of cyanoguanidine and 400 parts of 2-ethoxyethyl acetate, previously heated at reflux temperature for one hour. Refluxing was continued for another hour. The solution was then cooled and decanted from excess cyanoguanidine.

The resulting product was a colorless nearly clear solution of a polymeric material represented by the structure



where B is a MMA/BA/2-EHA terpolymeric segment.

A mixture of 1 part of this solution, 1 part of phthalocyanine blue and 8 parts of xylene was sandground. The resulting pigment dispersion showed excellent deflocculation.

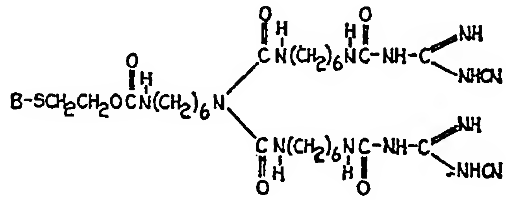
An automotive lacquer containing this dispersion gave a glossy film with excellent color development.

Example 8

A polymeric material was prepared according to the method of Example 7 by substituting 800 parts of ethyl acrylate (EA), 172 parts of vinyl acetate (VAc), 256

parts of BA, 23.4 parts of 2-mercaptoethanol and 4.9 parts of azobisisobutyronitrile in 800 parts of 2-ethoxyethyl acetate as the base solution in the initial part of the reaction.

The resulting product was a solution of a polymeric material represented by the structure

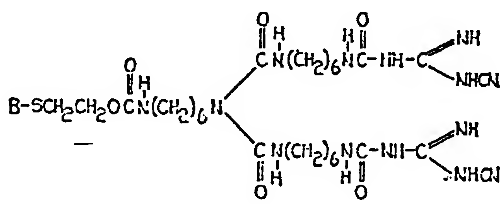


where B is an EA/VAc/BA terpolymeric segment.

Example 9

A polymeric material was prepared according to the method of Example 8, using an initial solution of 1000 parts of EA, 320 parts of BA, 169 parts of octadecyl methacrylate (OMA), 10 parts of tertiary butylperoctoate, 29.6 parts of 2-mercaptoethanol and 1000 parts of 2-ethoxyethyl acetate.

The product was a solution of a polymeric material represented by the structure



where B is an EA/BA/OMA terpolymeric segment.

Example 10

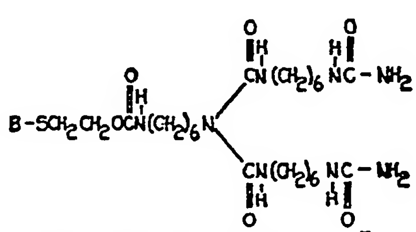
Toluene (226.7 parts) was placed in a steel reaction kettle. The toluene was heated to reflux temperature and held there while a solution of 226.7 parts of MMA, 126 parts of 2-EHA, 90.7 parts of toluene. 4.44 parts of 2-mercaptoethanol and 0.903 parts of azobisisobutyronitrile was added over a 4 hour period.

A solution of 0.25 part azobisisobutyronitrile in 2.5 parts of methylisobutyl ketone was then added in three equal portions at 15 minute intervals. A water separator was then attached and refluxing was continued for another 45 minutes to remove water.

To this reaction mass were then added 43.21 parts of Desmodur N. The Desmodur container was rinsed with 3.78 parts of toluene, which was also added to the reaction mass. The mass was stirred for 5 minutes and 0.51 part of dibutyltin dilaurate was then added and its container rinsed with 1.89 parts of toluene, which was also added to the mass.

The resulting solution was then refluxed for one hour. Ammonia was bubbled through a sample of the above solution at 25°C., with stirring, for 15 minutes. Excess ammonia was then purged from the mass with a stream of nitrogen.

The product was a solution of a polymeric material represented by the structure



where B is a MMA/2-EHA copolymeric segment.

Example 11

Methylethyl ketone (241.9 parts) was placed in a steel reaction kettle. The methylethyl ketone was heated to reflux temperature and held there while a solution of 219.9 parts of MMA, 131.9 parts of 2EHA, 66 parts of methylethyl ketone, 4.3 parts of 2-mercaptoethanol and 0.88 part azobisisobutyronitrile was added over a 4 hour period.

Refluxing was continued as a solution of 0.22 part of azobisisobutyronitrile in 4.2 parts of methylethyl ketone was added in three equal portions at 15 minute intervals. Refluxing was then continued for another 30 minutes.

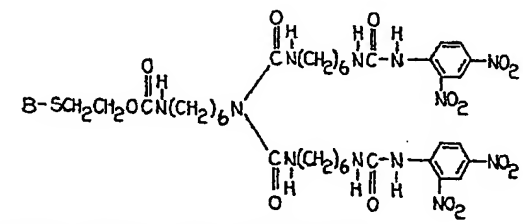
To this solution were then added 43.21 parts of Desmodur N. The container was then rinsed with 11 parts of methylethyl ketone which was also added to the reaction mass.

After this solution was stirred for 5 minutes, 0.5 part of dibutyltin dilaurate was added and its container rinsed with 4.4 parts of methylethyl ketone, which was also added to the reaction mass.

The solution was then refluxed for 2 hours.

This polymer solution (1200 parts) and 33.5 parts of 2,4-dinitroaniline were stirred and heated at reflux temperature for two hours.

The resulting product was a solution of a polymeric material represented by the structure

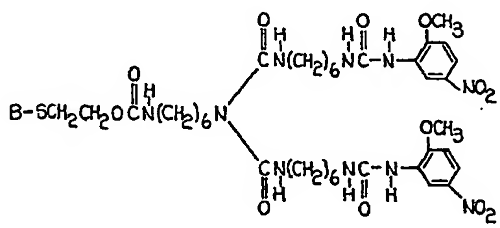


where B is a MMA/2-EHA copolymeric segment.

Example 12

A polymeric material was prepared according to the method shown in Example 11 by using 2-methoxy-5-nitroaniline in place of the 2,4-dinitroaniline.

The resulting polymeric product is represented by the structure

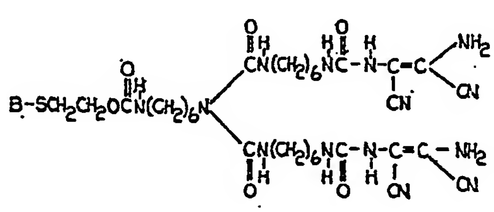


where B is a MMA/2EHA copolymeric segment.

Example 13

A polymeric material was prepared according to the method of Example 11 by using diaminomaleonitrile in place of the 2,4-dinitroaniline.

The resulting product was a polymeric material represented by the structure



where B is a MMA/2EHA copolymeric segment.

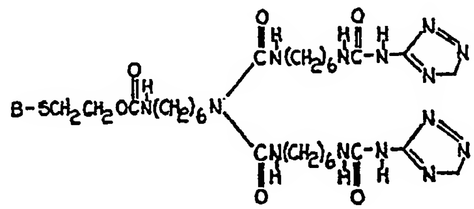
Example 14

To 1200 parts of the solution of the diisocyanate terminated polymeric inter-

mediate prepared in Example 10 were added 15.9 parts of 3-amino-1H-1,2,4-triazole and 310 parts of 2-ethoxyethyl acetate.

This mixture was stirred for 2 hours at 25°C. and then heated at about 100°C. until the solids dissolved.

The solution was then cooled to give a solution of a polymeric material represented by the structure



where B is a MMA/2EHA copolymeric segment.

Example 15

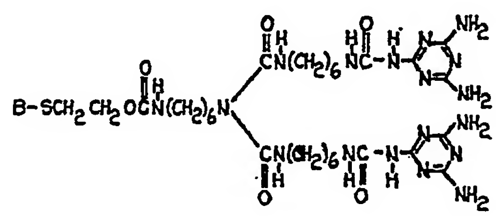
Benzene (250 parts) was placed in a reaction vessel. The benzene was then heated to reflux temperature and held there while a solution of 1000 parts of EA, 320 parts of BA, 169 parts of OMA, 30 parts of 2-mercaptoethanol and 8.2 parts of azobisisobutyronitrile in 950 parts of benzene was added continuously over a 5 hour period.

The resulting solution was concentrated on a rotary evaporator to give 1496 parts of a stiff, colorless oil.

Twenty-seven parts of this oil were dissolved in 100 parts of dimethylformamide and the solution mixed with a solution of 3.5 parts of Desmodur N and 0.1 part of dibutyltin dilaurate in 30 parts of dimethylformamide.

The resulting solution was then stirred at 140°C. for 3 hours and 1.6 parts of melamine added.

This solution was heated for another 2 hours at 140°C. and then poured into water. The oil which separated was washed with water, dissolved in tetrahydrofuran and dried under vacuum to give 19.5 parts of a glassy polymeric material represented by the structure

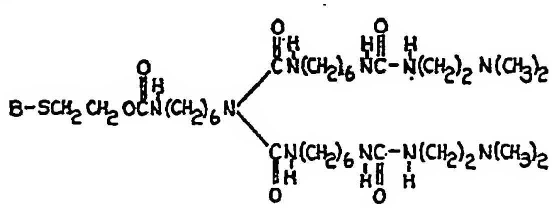


where B is an EA/BA/OMA terpolymeric segment.

Example 16

A mixture of 3008 parts of the isocyanate terminated intermediate polymer prepared in Example 1, 10.5 parts of 2-ethoxyethyl acetate and 54 parts of N,N-dimethylethylenediamine was stirred for 1 hour at room temperature and then held at 100°C. for 15 minutes.

The resulting product was a 50% solution of a polymeric material represented by the structure

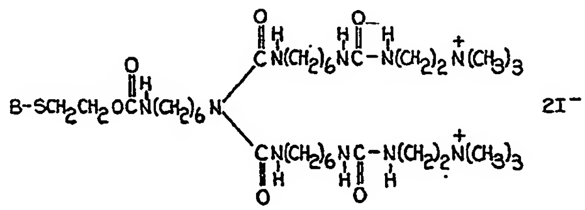


where B is a MMA/2-EHA copolymeric segment.

Example 17

The solution product of Example 16 (536 parts) was mixed with 22.8 parts of methyl iodide and 200 parts of methylethyl ketone at room temperature.

This mixture was allowed to stand for 4 days at room temperature. The resulting solution was then filtered through Celite (trade mark) to give a solution of a polymeric material represented by the structure

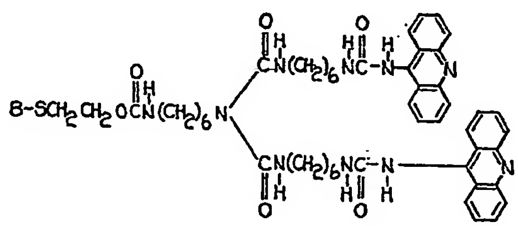


where B is a MMA/2EHA copolymeric segment.

Example 18

The isocyanate terminated intermediate polymer solution prepared in Example 11 (700 parts) was heated to reflux temperature and held there while a solution of 18.7 parts of 9-aminoacridine in 374 parts of methylethyl ketone was added. The mixture was then refluxed for another 15 minutes.

The resulting product was a solution of polymeric material represented by the structure



where B is a MMA/2EHA copolymeric segment.

The polymeric materials of Examples 7—18 can be used to prepare coating compositions in the same fashion as shown in Examples 1 or 2 with similar results.

WHAT WE CLAIM IS:—

1. A polymeric material represented by the structure

$$\left(B-X-\overset{O}{\overset{\|}{C}}-\overset{H}{N}\right)_m-Y-\left(\overset{H}{N}-\overset{O}{\overset{\|}{C}}-A\right)_n$$

where

B is a polymeric segment of one or more ethylenically unsaturated monomers lacking Zerewitinoff hydrogen atoms;

X is the residue of a chain transfer agent;

Y is the residue of a di-, tri- or tetraisocyanate radical;

A is an acid radical which is derived from an acid having a pk_a value of -1 to 6, or a basic radical which is derived from a base having a pk_a value of 5 to 14, or a salt of such a basic material, and

m and n 1, 2 or 3, (the total not exceeding 4); provided that when n is 2 or 3, only one of A need be as defined.

2. A polymeric material according to Claim 1 wherein A is a mercapto-, hydroxy- or carboxy substituted carboxylic acid radical.

3. A polymeric material according to Claim 2 wherein the carboxylic acid radical is

$$-S-\underset{\displaystyle H}{\overset{\displaystyle CH_2COOH}{\underset{|}{\overset{|}{C}}}}-COOH$$

$$-S-(-CH_2-)-_nCOOH \qquad \text{(where n is 1—3)}$$

$$-O-\underset{\displaystyle (CH_2)_5CH_3}{\underset{|}{C}}H(CH_2)_{10}COOH \quad ,$$

$$-O-CH_2CH_2\underset{\displaystyle CH_2CH_2N(CH_2COOH)_2}{\underset{|}{N}}-CH_2COOH$$

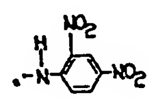
or

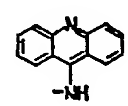
$$-(-CH_2-)-_{10}COOH$$

4. A polymeric material according to Claim 1 wherein A is an amino-, hydroxy- or mercapto substituted amine or amine salt radical.

5. A polymeric material according to Claim 4 wherein A is a radical of the formula

$$-NH_2 \qquad \qquad -\overset{\displaystyle H}{\overset{|}{N}}(NC)C=C(CN)NH_2$$





$$-\overset{\displaystyle H}{\overset{|}{N}}-\underset{\displaystyle HNCN}{\underset{|}{C}}=NH \qquad \qquad -\overset{\displaystyle H}{\overset{|}{N}}(CH_2)_2\underset{\displaystyle CH_2CH_2OH}{\underset{|}{N^+}}(CH_3)_2 \quad Br^-$$

or

$$-NHCH_2CH_2N\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

6. A polymeric material according to any of Claims 1 to 5 wherein B is a polymeric segment of
(a) an ester of AA or MAA with an alkanol of 1—18 carbon atoms;
(b) styrene or acrylonitrile;
(c) a vinyl ester derived from an acid of 2 to 18 carbon atoms; or
(d) a vinyl ether.

7. A polymeric material according to Claim 6 wherein B is a polymeric segment one of whose monomer units is MMA.

8. A polymeric material according to Claim 6 wherein B is a copolymeric segment of MMA and an ester of AA or MAA with an alkanol of 2—12 carbon atoms.

9. A polymeric material according to Claim 6 wherein B is a MMA/2EHA copolymeric segment.

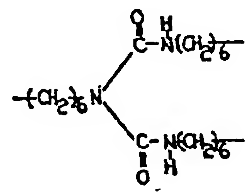
10. A polymeric material according to any of Claims 1 to 9 wherein X is

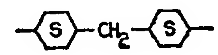
—S—R—D

where R is alkylene of 1—6 carbon atoms, and

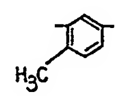
D is —O—, —S—, $-\overset{O}{\overset{\|}{C}}-O-$ or —NH

11. A polymeric material according to any of Claims 1 to 10 where Y is

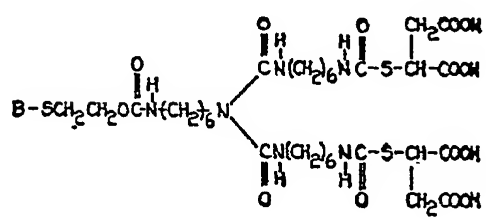




or

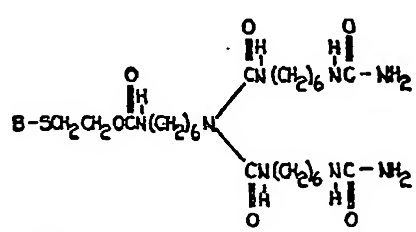


12. A polymeric material represented by the structure



where B is a MMA/2EHA copolymeric segment.

13. A polymeric material represented by the structure



where B is a MMA/2EHA copolymeric segment.

14. A polymeric material according to Claim 1 substantially as herein described in any of Examples 1 to 6.

15. A polymeric material according to Claim 1 substantially as herein described in any of Examples 7 to 18.

16. A dispersion which comprises solid particles dispersed in an organic liquid together with one or more polymeric materials as claimed in any of Claims 1 to 15.

17. A coating composition which comprises at least one polymeric material as claimed in any of Claims 1 to 15, an organic liquid, a film-forming polymer, and pigment particles dispersed in the liquid.

18. A coating composition according to Claim 17 substantially as herein described in any of the Examples.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.